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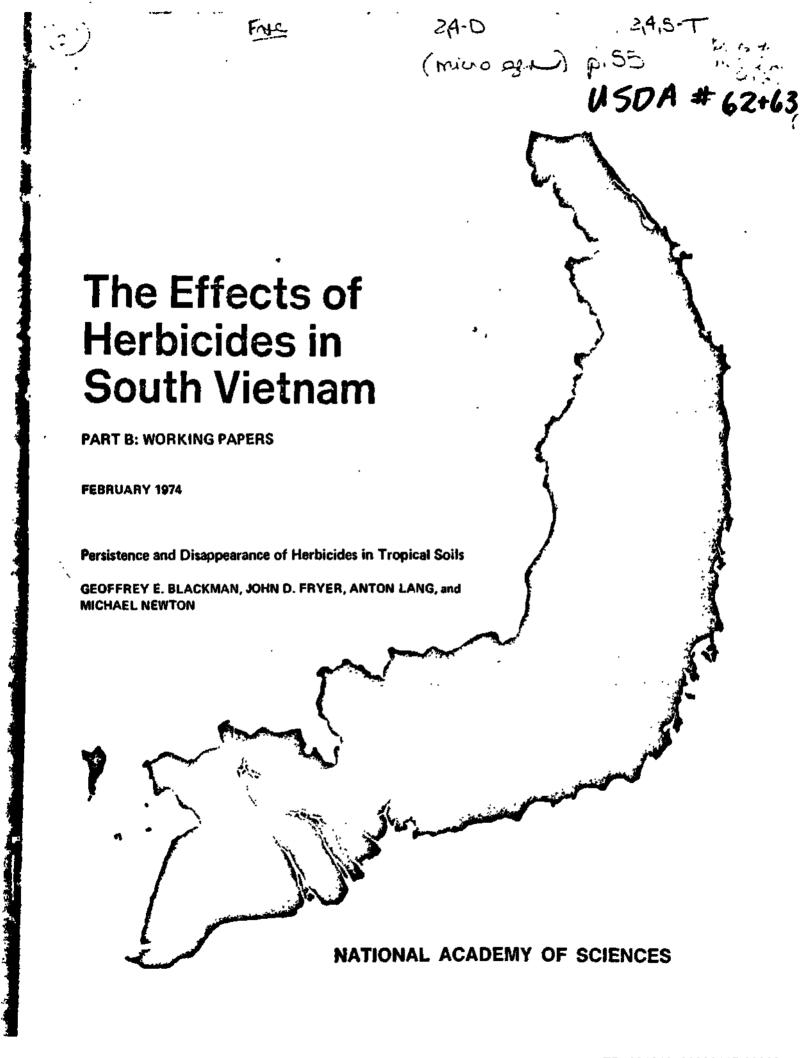
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THE EFFECTS OF HERBICIDES IN SOUTH VIETNAM

PART B: WORKING PAPERS

FEBRUARY 1974

Persistence and Disappearance of Herbicides in Tropical Soils GEOFFREY E. BLACKMAN, JOHN D. FRYER, ANTON LANG, AND MICHAEL NEWTON

NATIONAL ACADEMY OF SCIENCES - NATIONAL RESEARCH COUNCIL WASHINGTON, D.C. 20418

Persistence and Disappearance of Herbicides in Tropical Soils

GEOFFREY E. BLACKMAN, JOHN D. FRYER, ANTON LANG, AND MICHAEL NEWTON⁸

SCOPE OF WORK

A very obvious and legitimate question poses itself when an extraneous material has been introduced into the environment: how long will this material persist, or how fast will it disappear? Disappearance in this case means loss of its characteristic activity either in its original form or in the form of derivative(s). For the military herbicide operations in South Vietnam (SVN) this question is particularly obvious and urgent. Herbicides have been used in those operations at levels roughly five to ten times higher than in normal agricultural practice, and some areas were sprayed twice and more often, sometimes within a relatively short time. Where effects of defoliation persist, as in the mangrove forests, is it because the herbicides are still active, or because of other changes induced by the herbicides, even though the latter themselves may have disappeared?

In addition, claims have been made--in articles on the effects of the use of herbicides in the Vietnam war, in news reports, and

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elsewhere—that these compounds have "poisoned" the soil, rendering large areas incapable of supporting either indigenous or crop vegetation. Some of these reports convey the impression that vast parts of SVN are barren and will remain so for unknown but extensive periods of time. The term "ecocide," i.e., destruction of the plant and animal community on a large scale and in an irreversible manner, has been used.

The Committee therefore considered soil studies on persistence and disappearance of herbicides among its essential tasks. This task was approached in two ways.

First, on our forays into different parts of the country we collected soil samples in areas that had been sprayed operationally with herbicides during the Vietnam war. As far as possible, emphasis was placed on sites that had received high total doses of herbicides, since it seemed that the prospects of finding measurable residues would be highest at such locations. However, this collecting activity was greatly limited by security problems. Thus, only one inland forest site could be sampled, and it had received only two sprays. The total number of samples from operationally-sprayed areas was 48.

Most of the samples were subdivided into two or three parts and almost all of them were analyzed for two different herbicides, and some for three; hence, the total number of analyses was about 200. The Committee also collected some water samples from a river in the heavily-sprayed Rung-Sat Special Zone mangrove area.

Second, the Committee conducted a number of experiments in which the soil surface was sprayed with herbicides at a known rate equivalent to that used in a single operational spray mission. The

disappearance of the compound was then followed by sequential tests over a period of about 150 to 250 days. The reason for doing these experiments was that when the Committee started its work, one and a half years had elapsed since the termination of major herbicide operations. It was thus too late to observe the early stages of herbicide behavior in the soil. However, a knowledge of these early stages is very important if valid conclusions are to be reached about the course of the disappearance of the herbicides. In addition, it appears that where crops had been destroyed by herbicides, farmers were sometimes hesitant to replant, being afraid that the new crops would also be killed or damaged. The Committee was on several occasions asked when replanting would be safe. About 1000 soil samples were analyzed for herbicide content during this phase of the Committee's work. In addition, a series of biological tests to evaluate the rate of disappearance of herbicides was undertaken.

All herbicide experiments in SVN were conducted with the authorization of the GVN and, where appropriate, of the proper local authorities.

^aThe Committee also conducted an experiment in which two strips of mangrove, each 400 ft (100 m) long by 120 ft (30 m) wide and totalling less than 2 acres, were sprayed by helicopter with Agent Orange and Agent White, respectively. The objectives were to study the early responses of the plants, to determine differences in sensitivity, and to investigate the behavior of the herbicides in the soil under conditions comparable to those of wartime herbicide operations (or, more exactly, to follow up the consequences of the first herbicide application to vegetation). However, this experiment failed; the sprayed vegetation exhibited only minimal symptoms of damage and thuse had almost completely disappeared seven months later. The reasons are not entirely clear. herbicide batches used were the same as those that proved very effective when sprayed by hand on soil. Most probably, the equipment, which had not been in use for quite a long time, was not functioning properly and did not deliver the specified amount of herbicide. No analyses for herbicides were done from these plots.

work. Biological determination was used primarily in the experiments with agricultural crops and soils because here the advantage of this method, as just mentioned, is particularly evident. If a plant does not show measurable effects six months after application of a herbicide to the soil, it can be concluded that this particular plant, if resown, will remain undamaged in future plantings, provided cultural and environmental conditions are not appreciably changed. The test plants that were chosen for the Committee's experiments were rice and other crop plants of considerable present or potential value in SVN and other tropical countries. Biological measurements of herbicide effects on mangrove seedlings were also carried out. Serial plantings were made in order to determine how long herbicides have direct adverse effects on mangrove seedlings, and also to obtain some information on conditions for reestablishment of the mangrove.

The first chemical determinations were carried out by the Weed Research Organization, Yarnton, Oxford, England. Subsequently, the analytical work was conducted under a subcontract with the Huntingdon Research Centre, Huntingdon, U.K., an organization with considerable experience and an excellent reputation for this kind of work. The analyses were made mainly for 2,4,5-T, one of the compounds in Agent Orange, and for picloram, one of the compounds in Agent White, because all experience indicates that these are more stable than 2,4-D (which is present in both Orange and White). 2,4-D was determined only in selected samples, usually those with a high content of either of the other two compounds. The analyses were carried out by means of electron capture gas chromatography. The methods used were the most up-to-date standard

residue procedures available and have been proved in several different laboratories. For picloram a basic extraction followed by esterification with diazomethane (McKone and Cotterill, unpublished) was used; for 2,4,5-T the residues were extracted into an organic solvent and then the n-butyl ester (McKone and Hance 1972) was the preferred derivative. Following routine procedure in herbicide work, all results are given as acid equivalents, disregarding the moiety of the molecule that forms the ester. The results for soils are expressed as lb/acre of soil surface, i.e., as if all herbicide in a sample (or subsample) was deposited on the surface of the soil. Water samples are reported in parts per million (ppm). Values preceded by a < mean that no herbicide could be detected at this level of sensitivity. It will be seen from the results that the limit of detection varied to some extent from one batch of samples to another. This was because of slight changes in the sensitivity of the electron capture detector over a period of time, and in a few cases also because of varying amounts of material available. (If these amounts drop below a certain limit, the sensitivity of the analytical methods decreases.) The accuracy of the results was ensured, however, by the inclusion of some analytical standards with each set of samples.

To check the reliability of the determinations, a random selection of samples with high, medium, and low herbicide levels was analyzed by the Gulf South Research Institute, New Iberia, Louisiana: the comparative results are shown in Table I. It can be seen that at low concentrations, near the detection limit, the agreement between the two determinations was generally good; at higher concentrations, the values found for the two forest soils by GSRI were considerably lower than those of HRC. In our evaluations we used the HRC data, since their results for control tests (samples taken immediately after spraying) were--

Table I.

Comparative determinations of 2,4,5-T and picloram in soil samples by Huntingdon Research Center and Gulf South Research Institute.

Data in ppm. < = below this detection limit. ND = not detected.

	ŷ <u>"</u>	Sample	2,4,	5-T	Picloram			
ro-	Soil .	No.	HRC	GSRI	HRC	GSRI		
garding	Mangrove (Vung-Tau, SVN)	1	2.99	3.293	0.44	0.260		
ė		2	1.28	1.114	0.342	0.102		
		3	0.59	0.51 0	0.047	0.032		
e (or		4	0.26	0.096	0.04	0.012		
ported		5	0.06	0.049	0.004	0.003		
2 • • • • • • • • • • • • • • • • • • •		6	0.03	.0.016	<0.004	ND		
œ								
results	Mangrove (Rung Sat)	1	0.03	0.005	<0.002	ND		
		2 .	0.013*	0.005	<0.002	ND		
es to		3	<0.02	0.005	<0.001	ND		
ectron		4	<0.005 ^{&}	0.005	<0.001	ND .		
:	Forest (Ban-Me-Thuot,SVN)	1	3.16	0.412	0.402	0.115		
-4 4 ···	20,000 (2000 100 2000 1,000)	2	0.58	0.245	0.060	0.041		
tain .		3	0.02	0.016	0.003	ND		
7		•	V.V.	01010	V.V			
1	Forest (Los Baños,	1	8.09	0.332	1.265	0.132		
1	Philippines)	2	1.13	0.079	0.03	0.003		
1		3	0.02	0.011	0.005	ND		

*Analyzed by Weed Research Organization

Note: The samples for 2,4,5-T and for picloram are not always identical

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with a single exception--very close to the theoretical values. (The GSRI analyses did not include such control tests.)

Soil Sampling

Soil sampling was done in two ways. Surface samples were collected mostly with the aid of metal (iron) cans, 5 in. (12.5 cm) high and of the same diameter, which were pushed into the soil and then extracted with the aid of a spade. This procedure was mainly used with mangrove soils, since they are soft enough to permit complete insertion of the can. Deeper samples, which will be called cores, were collected with soil samplers specially constructed by the Weed Research Organization. Two different but similar samplers were used, both consisting of a metal tube with sharpened bottom edges, either 2 in. (5 cm) or 1.75 in. (4.4 cm) wide and either 36 in. (90 cm) or 30 in. (75 cm) long. Both samplers were provided with strong, interchangeable metal caps: one plastic-covered to minimize damage when driving the sampler into the soil, the other provided with handles to extract it again. There were also removable split inside liners for extracting the cores, but these proved to be of limited value and the cores were usually pushed out of the sampler tube with a metal rod with a disk at one end. When muddy soil (mangrove) was collected, an adjustable air vent at the upper end of the sampler tube was left open while inserting the sampler into the soil, to permit escape of air. The vent was closed, or the upper opening of the tube simply plugged with a rubber mallet, when the sampler was extracted, thus generating a vacuum that helped keep the soil in the sampler tube. Sometimes, a metal tube with a metal rod inside was pushed into the mud next to the sampler and

the rod then withdrawn; this permitted air to penetrate to the end of the sampler, relieving a vacuum and facilitating the extraction of the sampler. In many cases, both with hard forest soils and with soft mangrove mud, the sampling proved an arduous and time-consuming task, and despite all precautions the contained cores were often considerably shorter than the length of the sampler because part of the core slipped out of the sampler and/or because the friction between the soil and the wall of the sampler tube either caused the core to compact or prevented the soil from entering the tube beyond a certain point.

Wherever soil samples were collected, some control samples were taken from areas that had not been exposed to herbicides. These controls served to ascertain whether the soil contained natural materials interfering with the determination of the herbicides. If this was so, the analytical procedures were modified so as to exclude such sources of error. Criteria used for choosing the control sites were: information on herbicide missions in the area (printouts from the HERBS tape and, where available, information from local military personnel); condition of the vegetation; and information from the local population (village and district officials, and farmers or woodcutters). In the mangrove, where sprayed areas exhibit pronounced damage and often complete kill of the mangrove trees, identification of control sites was not difficult. Good local information faciliated location of the forest sites at Pran Buri, Thailand, and Cau Muoi-Mot, SVN, as well. In other locations, the identification was a good deal less reliable, and it appears that some of the control sites had been exposed to herbicide, too.

The surface samples were stored in the cans, which were closed with their lids. The cores were in most cases divided into two or three parts and placed either into double polyethylene bags or, more commonly, into plastic jars with airtight screw caps. In the case of mangrove soils, which are highly anaerobic (i.e., lacking in air and perticularly in oxygen), care was taken to fill cans and jars to the rim and to tape the lids of the metal cans with masking tape, thus reducing exposure to air, which might cause changes in the soil and thus also affect herbicides still present in it. The samples from SVN and the Philippines were stored in a deep freezer and shipped for analysis in frozen condition. All effort was made to complete these safety procedures as rapidly as possible, and in most cases the samples were placed in the deep freezer on the evening of the day of sampling or on the next day. However, particularly in the earlier part of the Committee's work, this was not always possible and samples occasionally had to remain unfrozen for as long as one week. In some cases, 1t was possible to keep them part of this time in a refrigerator.

Water samples were kept in plastic containers in the dark to prevent breakdown of herbicides by light. Some formalin was also added to prevent decompostion by microorganisms.

HERBICIDE DETERMINATIONS IN SOILS AND WATER FROM DEFOLIATED SITES
Sites

The sites that have been subjected to herbicide sprays in connection with the Vietnam war and from which the Committee took soil samples are listed in Table II. Two were in an area in Thailand that had been

Location, herbicide spraying history, and soil sampling information for land sites that had received herbicides during military operation.

Table II.

Location - (SVN, unless otherwise noted)	Date	Spray history Agent	Amount	Date	No. & type of samples
Forest, Pran Buri, Thailand: herbicide spray test site, Plot 28	June 1965	Orange + picloram	9.1 lb/acre 0.5 "	Sep 30,1971	8 cores (2 sa. from 4 sites) ca. 16-26 in., divided in upper organic part (ca. 6 in.) and remainder
Calibration Grid, Pran Buri. Thailand	1964 -65	Purple brink broad Cacadylic acid (>Blue) Picloram total of ca. 840 960 lb 2,4,5-T; 57 lb cacadylic picloram per acre	128 1b dicamba; acid, 20 1b	Oct 1,1971	6 cores, ca. 26-32 in., 3 ea. from a bare (Nos. 1-3) and from a grass-covered (Nos. 4-6) area and 2 from an area supposedly outside the grid (No. 7,8): all divided into 3 equal sections (T-top, M-middle. B-bottom)
Crop land: dump site near Chieu-Lieu Hamlet Tan- Dong-Hiep Village Di-An Distr., Bien-Hoa Prov.	Dec 1, 1968	1000 gal. Orange dumped on circular path from 1800 ft.		Oct 8, 1971	4 cores, ca. 28-35 in. divided into 3 approx. equal sections (T,M,B)
Forest: Cau Muoi-Mot strongpoint, ca.8 mi. (12 km) north Dong-Koai Village, Don-Luan Distr., Phuoc- Long Prov.	Dec 1, 1968 Apr 12,1969		3 gal/acre 3 *	Oct 16, 1971	4 cores, ca. 33-34 in., divided into 3 equal sections (T,M,B)

Table II, continued

Location - SVN (Unless otherwise noted)	_	y history Gent	' Amount	Date	No. & type of samples				
Mangrove, Rung Sat Special Zone					·				
Site #1	Mar 1, 1965 Oran Jan 6, 1966 Oran Nov 11, 1967 Oran Aug 3, 1968 Whit	nge nge	3 gal/acre 3 " 3 "	Oct 9, 1971	<pre>3 surface samples, depth not determined, = RS-1 through ~3</pre>				
	Aug 4, 1968 Oran Aug 7 1968 Blue Aug 8, 1968 Oran Aug 9, 1968 Whit	nge e nge	3 " 3 " 3 "	Mar 9, 1972	2 cores, 36 in., divided into 3 equal parts (T,M,B) = RS-4 and -5				
	Aug 18, 1968 Oran = minimum of 86 79 lb 2,4,5-7 3 lb picloran 9 lb cacodyli acre; compare	nge 6 1b 2,4-D; T; m; ic acid per	3 *	Aug 31,1972	6 surface samples (5 in,) and 6 cores (ca. 30 in.) from same sampling sites divided into 2 equal section (T,B) = RS-6 through -11				
Site #5				Aug 31,1972	6 samples same as Site #1 31 Aug 72 - RS-12 through -17 S,T,B				
Site #6 Site #7 Site #8			}	Aug 31,1972	One sample each, same as Site \$1, Mar 9, 1972 (T,N,B) ~ RS-18 through -20				

Table II, continued.

Location - SVN (Unless otherwise noted)	Date	Spray history Agent	Amount	Date	No. & Type of Samples
Mangrove, Ca-Mau Peninsula: Ca. 9-45 yd both sides of airstrip at Nam-Can Vill- age, Nam-Can Distr An- Xuyen Prov:	July 1968	Orange	?	Oct 1 , 1971	3 samples each consisting of several cores, ca. 36 in which had been divided into 3 parts: 6 in6 in remainder (T-M-B); plus one sample 12 in. only: T and M
Cs. 3 mi. north-northeast of Nam-Can Naval Base, west bank of Kinh-Ngang canal	on bound		3 gal/acre 3 " 3 " 3 "	Oct 12, 1971	3 samples as in Ca-Mau Peninsula, above

The figures are the depth of the hole. The length of the core was often considerably less, due to compacting and/or friction preventing the soil from entering the sampler. This was particularly marked with many mangrove samples.

b Agent Pink = 60% 2,4,5-T-n-butyl ester 40% 2,4,5-T-isobutyl ester

C Dicamba = 3,6 dichloro-o-anisic acid (controls certain phenoxy tolerant broadleaf weeds and brush species)

used for extensive trials with different herbicides in 1964-65, prior to large-scale use in SVN. No herbicide symptoms were seen on native plants, crops, or weeds. Samples were collected from one of the few trial plots that could still be definitely located (Plot No. 28), and from the center of the so-called Calibration Grid. The latter is an old rifle range at the Pran Buri Training Center, and all treatments that were used in the individual trials had been sprayed over this site. The direction of the sorties was at varying angles according to wind, but all intersected in a central area that, at the time of the Committee's visit, still stood out clearly because of several large patches of completely bare soil or very restricted vegetation, mostly grasses (Imperata and others). This site had received truly formidable quantities of some herbicides, e.g., 70 times more 2,4,5-T and almost as much more 2,4-D as delivered on one regular herbicide mission with Agent Orange (or 140 times as much 2,4-D as on one Agent White mission).

In SVN, the Committee was able to take soil samples in a so-called dump area, i.e., an area where, because of engine or other trouble, a plane delivering herbicides had released (dumped) the entire load over a relatively small area. The sampling site, which was in an area presently under crops (at sampling time, mainly peanuts), was originally located from the report of the pilot of the dumping plane and was subsequently verified by interviews with district and village officials and with villagers. It was definitely within the perimenter of the dump, although probably nearer its edge than its center. At the time of the Committee's visits, many dead trees--mostly fruit trees--could be seen, either still standing or, more frequently, felled and cut for firewood.

Some fruit trees had dead branches that may have been the result of herbicide damage, although the trees had produced new growth and were bearing some fruit. Some tall, unidentified trees looked quite normal, however, suggesting that the dose of herbicide had not been excessively high as compared to regular herbicide missions. (The dump was made from a height of 1800 ft or 540 m, as compared to the 150 ft or 60 m of the regular defoliation mission.)

The one inland forest site that could be sampled in SVN had been subjected to one Orange and one White mission. The area had been heavily disturbed by long-term human activity; only a thin stand of large trees and much old bamboo were present, and the trees were either dead or exhibited clear herbicide damage.

In contrast, a relatively substantial number of samples were collected on several trips to the central part of the Rung-Sat Special Zone, in a mangrove area that has received more herbicide sprays than any other region in SVN. One site, our #1, had been within the recorded flight lines of nine missions and received six times as much 2,4,5-T and seven times as much 2,4-D as a single Agent Orange mission, or about 14 times the amount of 2,4-D as a single Agent White mission. Moreover, these are minimum values; no less than 24 other missions had passed near the site between January 1966 and September 1968, and the site had almost certainly been reached by additional herbicide--if not directly, then by drift. The level of herbicide exposure of the other sampling sites in the Rung-Sat mangrove was undoubtedly similar. In the mangrove of the Ca-Mau Peninsula, the southernmost tip of the country, samples could be taken from two sites. One of these, situated close to the Nam-Can

Naval Base, had been hand-sprayed with Agent Orange. Date(s) and amounts are not known, but since some of the mangrove plants showed regeneration, the level was probably not higher and perhaps somewhat lower than from an aircraft spray. The second site, on the Kinh-Ngang Canal about 3 miles (4.8 km) northeast from the first, had received a spray with Agent Purple, a precursor of Orange, in 1962, and two White and one Orange sprays in March-April 1970. The sampled area was entirely devoid of live mangrove trees but was covered in parts by a creeping grass (Paspalum sp.).

As far as possible, sampling was done according to some pattern aimed at a uniform distribution over the accessible area that also included different parts of it. For example, in some of the mangrove sites completely bare areas were examined along with areas covered with grass (mai Paspalum vaginatum) and bearing some mangrove seedlings. Sometimes, however, e.g., in the Cau Muoi-Mot forest, the accessible area was so small that sampling had to be done at random.

Water samples were taken on two occasions in the lower part of the main shipping channel to Saigon that runs through the Rung-Sat Special Zone, beginning at our land site RS #1 and going south on the Dang-Xay, Mu-Na, and Dong-Tranh Rivers. Some control samples were collected in a small channel near our experimental sites in the mangrove of Chi-Linh near Vung-Tau (see below). The sites of the second Rung-Sat samplings, made on August 31, 1972, are shown in Figure IV C-5, Section IV, Mangrove Forests, Part A of the Report on the Effects of Herbicides in South Vietnam. No precise record was kept of the first sampling occasion in the Rung-Sat, but the area was similar to that of the second occasion. All samples were

taken at outgoing tide and near the water surface.

Results: Soil Samples

Results of the soil analyses are summarized in Table III. Substantial levels of picloram and 2,4,5-T, sufficient to prevent growth or to cause serious malformations in many broadleaf plants, were present six years after application in some of the soil samples from the Calibration Grid in Pran Buri, Thailand. Picloram was found throughout the length of the cores, but except in one (out of six) the concentrations in the bottom third (20 to 30 in. or 50 to 75 cm) were low. 2,4,5-T was found in the top and middle thirds (top, 0 to 10 in. or 0 to 25 cm; middle, 10 to 20 in. or 25 to 50 cm) in one sample, and in the top third in three samples; none was found in the bottom thirds.

Residues of both 2,4,5-T and picloram were also found in some soil samples from the Rung-Sat mangrove. Sample Site #5 (samples RS #12-17) seemed to contain 2,4,5-T consistently, particularly in the subsurface (below about 15 in. [38 cm] and to about 30 in. [75 cm]). No detectable amounts of picloram were found at this site to the depth that could be reached with the soil samplers. Some samples at Site #1 (samples RS #1-11) contained 2,4,5-T or picloram, and picloram but no detectable 2,4,5-T was present in the single samples from Sites #6, #7, and #8 (samples RS #18-20). In Sites #1 and #2, presence or absence of vegetation--including some mangrove seedlings--at the sampling sites seemingly was not linked with the variation of herbicide content in the soil. All herbicide levels found in the Rung-Sat mangrove soil are below those that can be expected

Table III. Herbicide residues in the soil samples of Table II, in lb/acre.

- * not sampled or analyzed. = below detection limit. S/T = surface samples or top portions of cores, B = bottom portions of cores.

Site Samp	ole No.	s/T ,	4-D B	2, ¹ S/T	+,5-T D	Picloram S/T B			
Forest, Pran Furi Flot 28	1-8	-	-	< 0.005 ⁸	∠0.005 ⁸	<0.001 ^a	<0.001 ⁸		
Calibration Grid, Pran Buri	12345678	<0.07 <0.08 <0.06 <0.06 <0.07 <0.08	<0.06 <0.06 <0.06 <0.06 <0.06	<0,03 1.35 0.96	0.03 0.03 0.03 0.23 0.03 :0.03	1.03 0.43 0.72 0.60 0.24 1.09	0.003 <0.003 0.008 1.19 0.004 0.01		
Dump Site, Di-An Distr. B	1-4 ulked	ح (٥٠٥ _٩ b	< 0.04°	<0.005 <0.005 ^d	<0.005 -	-	:		
Forest, Cau-Muoi-Mot	1-4	_	-	<0 .00 6	_0.006	<0.001	<0.001		
Mangrove, Site #1 Rung-Sat Site #2 Site #6 Site #7 Site #8	RS-1 RS-2 RS-3 RS-4 RS-5 RS-6 RS-7 RS-10 RS-11 RS-12 RS-13 RS-14 RS-15 RS-16 RS-17 RS-18 RS-19	40.007 40.04 40.04 40.04 40.04 40.04 40.007 40.007 40.007	<0.04 <0.04 <0.007 <0.007	0.010 ^d 0.013 ^d <0.005 ^d <0.006 <0.04 0.09 <0.02 0.19 0.21 <0.03 0.015 <0.01 0.24 0.02 <0.01 0.015	0.008 0.035 0.036 0.079 0.031 0.032 0.032 0.032 0.179 0.023 0.057 0.109 0.146 0.037 0.006	<0.001d <0.001d <0.001d <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.004 <0.005 0.006	0.002 < 0.004 < 0.004		
Mangrove, Nam-Can		. 0.001	i	<0.005 ^d ,	c/o 00=e		-		
Airstrip Canal Kinh- Ngang	1-3 1-3	- -0.030	3		<0.02ª	<0.001 ^d	<0.001 ^d		

analyzed analyzed

dValues in ppm since surface area of b3 samples, bulked c4 samples, bulked sample not known and therefore computation of lb/acre rate not possible
el samples

to cause damage to crops in normal agricultural practice.

No herbicide residues could be detected in the samples from Pran Buri Site #28, the dump site in Di-An District, the forest near Cau Muoi Mot, and the two mangrove sites in the Ca-Mau Peninsula. The failure to find detectable herbicide in the second Ca-Mau site (at the Kinh-Ngang Canal) is interesting insofar as this site had been sprayed relatively late in the war, one and a half years before our sampling.

Results: Water Samples

Water samples from the lower part of the main shipping channel to Saigon were analyzed for picloram, the most persistent of the herbicides used for military purposes in SVN. Suspended sediment--mostly soil--was separated from the water by filtration, and the two fractions were analyzed separately. As Table IV shows, no herbicide was found in the filtered water, but the sediment of four out of eight samples contained amounts ranging from about 0.07 to 0.03 parts per billion (ppb) of water and from about 2.2 to 0.8 ppm of dry weight of sediment. If all the herbicide in the sediment were to become available in the water, the levels would be far below the concentrations known to affect even the most sensitive species, but if only the sediments are considered, the levels are somewhat higher than those found in the Rung-Sat soil (maximum 0.01 lb/acre = 0.05 ppm). Herbicide in water is usually associated with suspended material if such is present, and turbid water may contain more herbicide than clear water, but the relatively high picloram content in the Rung-Sat sediment is somewhat unexpected.

Table IV.

Analyses for picloram in water samples from the Rung Sat. Values in ppm. ND = not determined

Location and w		Concentration	Concentration in sediment							
sampling site	no.	in filtered water	Computed for water	Computed for sediment (dry weight						
Vung-Tau, No.	2	ND .	<0.00002	<0.11						
Rung Sat, No.	4	ND	<0.00003	<0.17						
No.	5	ND	<0.00002	<0.24						
No.	6	ND	<0.00002	<0.50						
No.	7	<0.0001	0.000043	1.26						
No.	8	<0.0001	0.000036	1.06						
No.	9	<0.0001	0.000066	2.24						
No.	10	<0.0001	0.000029	0.77						

EARLY STAGES OF HERBICIDE BEHAVIOR IN SOIL UNDER TROPICAL CONDITIONS

This section summarizes the Committee's own experimentation on persistence and disappearance of herbicides in certain tropical soils.

Arricultural Sites

In all experiments with agricultural lands, the soil, previously cleared of any vegetation, was sprayed with either Agent Orange or Agent White at the rates of (1) three gal/acre (the rate used on most military spray missions, (2) one gal/acre, and (3) one-third gal/acre. The agents, as manufactured, are much too concentrated to permit accurate dosage for the relatively very small plots treated in all our experiments. and therefore they were diluted. In the case of Agent Orange, which is insoluble in water, an aqueous emulsion was made with the aid of special emulsifiers. Agent White is water soluble, and the necessary additional amounts of water were added directly to the commercial preparation. application was by means of a carefully calibrated backpack sprayer and a spray boom designed to ensure a uniform pattern of distribution (constructed by the Weed Research Organization). All spraying was carried out by one and the same person (except in the mangrove microplot experiment). Comparable plots were left unsprayed as controls. None of the plots had been treated with herbicides before our experiments.

Beginning some weeks after the herbicide application and at regular intervals thereafter, selected crops were sown or planted and their responses observed about one month later (in the case of paddy rice, additional data on total yield were taken after the plants had matured).

Weeds were controlled during and between plantings by hand, and in the

Philippines experiments also by application of a different herbicide: paraquat. Fertilizer was applied according to locally-established needs: during plantings, light surface cultivation was applied to the soil. The main characteristics recorded were number of surviving plants: height and wet weight either of all plants on a plot or of a number of plants selected at random; number of leaves and, for paddy rice, of tillers (side shoots emerging near the ground); plant color; and symptoms of herbicidal injury. Estimates of general vigor (on a scale of 0 to 10) and of ground coverage (i.e., the portion of a plot covered by the foliage of the crop, in percent) were also made for some plantings. In general, the most useful measurements -- since they provided the clearest indication of herbicide effects or their disappearance--were survival, plant weight, and degree of herbicidal damage). In the case of paddy rice, the plants were grown to maturity and the yields of air-dried grain determined. The results are expressed as the time, in weeks, from the date of the herbicide application to the date of that planting in which no effects on the growth of the plants, as determined by survival and weight, were noted, and if these times are different, also the time from herbicide application to the date of that planting in which any herbicide symptoms had disappeared. procedure is illustrated by Table V, which contains data for two. species that are relatively susceptible or resistant to the herbicidal agents, and by Figure 1, which is derived from these data.

Two experiments were carried out, one in the Philippines and one in SVN. The Philippines experiment was conducted on the experimental farm of Tropical Agri-Search, Makati, Rizal Province, Philippines at

22 weeks

Table V.

Survival, growth and herbicide symptoms of maise and peanuts grown in soil treated with 3--1--1/3 gal/acre of Agents Orange and White at different times after application. (Experiment at Alabang, Third Series.)

Survival and growth (fresh weight after 4 weeks) are expressed as percent of controls (plants grown on non-treated plots), symptoms on a scale from ++++ (very heavy) to 0 (absent).

Interval between		Agent Orange		Agent White					
raying soil	Surviving Plants	Plant Weight	Rerbicide Symptoms	Surviving Plants	Plant Weight	Herbicide Symp			
inting	1/3 1 3	1/3 1 3	1/3 1 3	1/3- 1 3	1/3 1 3 (Gallons per acre)	1/3 1			

									Maize									
4 weeks	96	84	89	96	126	138	0	0	0	109	129	64	60	83	51 ^{&}	0	0	ó
15 weeks	102	112	115	123	148	143	0	0	0	67	81	89	69	83	96	Ö	0	0
	4		·		,											_		
							_	P	eanut									
4 weeks	102	100	40 ⁴	69	101	99	+	++	+++	304	36 4	0.4	50 2	53ª	-	***	++++	-
15 weeks	148	102	128	124	115	128		0	0	106	133	133	95	117	112	0	+	+

⁴ Difference from control statistically significant.

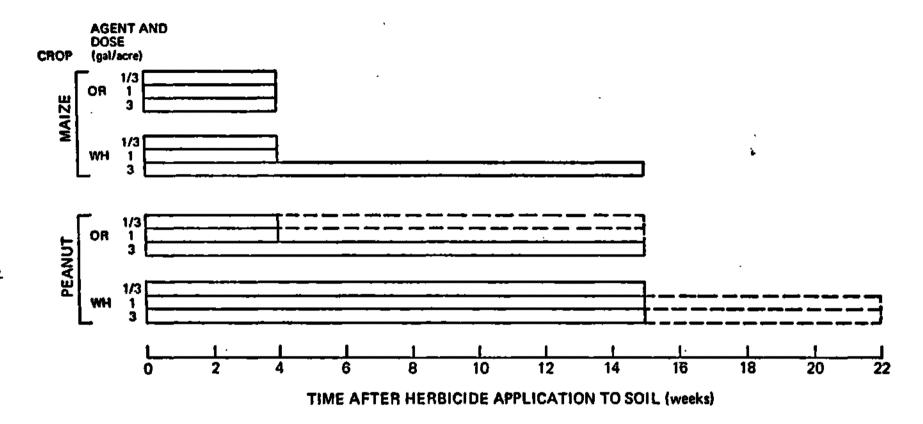


FIG. 1. Persistence of herbicide effects in maize and peanut (graphic representation of the results in Table V). The solid bars show the time between herbicide application to the soil and that planting in which effects of the herbicides on survival and growth (as fresh weight) were no longer present. The broken bars show that time after which no herbicide symptoms were evident. Lack of a broken bar means that herbicide symptoms were not present at all, or that they disappeared at the same time (i.e., in the same planting) as effects on survival and growth. Thus, the effects of Agent Grange (OR) on maize were no longer present in the planting made 4 weeks after herbicide application; those of Agent White (WH) at 1/3 and 1 gal/acre were not present in the same (4-week) planting and those at 3 gal/acre in that planting after 15 weeks. (Maize, as well as other cereals and grasses, exhibits few if any of the herbicide symptoms found in broadleaf plants, such as twisting of stems and leaves, reduction of the leaf blade, curling of leaf margins.) Effects of Agent Grange on survival and/or growth of peanuts on soil treated with 1/3 and 1 gal/acre were no longer present in the 4-week planting, but herbicide symptoms remained present until the 15-week planting, while on soil treated with 3 gal/acre, effects on survival (and herbicide symptoms) were present until the 15-week planting, but both had disappeared in the 22-week planting. In peanuts grown on Agent White-treated soil, effects on survival and growth were no longer present in the 15-week planting; and herbicide (picloram) symptoms on soil treated with 1 or 3 gal/acre disappeared in the 22-week planting.

Alabang, near Manila, under a subcontract with the International Rice Research Institute, Los Baños, the Philippines. The experiment onsisted of two parts; one for paddy rice and one for "dry crops" imize, sorghum, sweet potato, mung bean, peanut).

The rice was planted in 82 by 66 ft (25 by 20 m) paddies, three inlides were used for each of the two agents (Orange and White), and each inlide was subdivided by bunds into four sections for the three dose levels (3, 1, and 1/3 gal/acre) and an untreated control. Thus, each treatment was replicated three times. Flooding was arranged in such a way that water could not move from one plot to another.

The dry crops at Alabang were arranged in three different series. in one series, the herbicide application was made on February 2, 1972, uring the dry season, and the first planting occurred on February 25, 1772. Plantings were repeated at six-week intervals; all plantings were irrigated by soaker hoses and hand watering as long as the dry season 'asted. In the second series, the herbicide was applied at the same ime as in the first (February 2, 1972), but the plot was allowed to remain fallow until the onset of the wet season. Finally, in the : ird series, herbicide application was delayed until the wet season and was carried out on May 3, 1972. The first plantings in the second und third series were then made on May 30, 1972, simultaneously with the ideal in the first series (which had to be delayed one week ...ause of heavy rains). The objective of this threefold setup was to witain some information on the persistence of the herbicides in the alsence of rain. One planting (July 16-17, 1972) was partly lost in a bravy typhoon on July 19-20 and was therefore repeated on August 12-14,

resulting in a disruption of the schedule. The heavy rains caused losses of topsoil and may have thus caused some loss of herbicide as well. However, a careful inspection of the pattern of herbicide symptoms in the most sensitive crop of this experiment—peanuts—gave no indication of cross contamination of the different agents and dosages. The number of replicates in each of the three series was three for the controls (no herbicide) and two for each of the three herbicide levels. Reduction to two replicates was necessary because of the restricted area available.

The experiment in SVN was conducted at the Ea-Kmat Agricultural Research Station at Ban-Me-Thuot, Carlac Province, with the authorization of the GVN and the Director of the Agricultural Research Institute of the Ministry of Agriculture of the RVN, Dr. Thai-Cong-Tung. It was most capably supervised by the Manager of the Station, Ing. Nguyen-Van-Thoi, and his staff, in particular Ing. Truong-Duc-Bao. This experiment was restricted to crops capable of growth when receiving only natural rainfall The individual herbicidal treatments and the controls consisted of three replicates. The crops were dry (upland) rice, maize, sorghum, sweet potato, mung bean, and peanut. Because of poor germination and growth of sorghum during the first two plantings, and because herbicide effects had mostly disappeared by that time, sorghum was replaced by soybean after these plantings. Rice, mung bean, and soybean suffered heavily from insect attack and the data obtained were less complete than for the other crops; nevertheless, comparisons between plants on herbicide treated and untreated plots were possible in most cases. The herbicide applications were made on March 24, 1972, at the normal starting time of the rainy season. The first planting was on April 22, and subsequent

plantings were made at intervals of six to seven weeks, with the last one (for Agent White-treated plots only) on October 25, 1972. As the rainy season in 1972 began unusually late and was relatively short, and as no irrigation system was available, the first and last plantings suffered from drought. The growth of the first two plantings was impaired by a heavy growth of weeds.

The soil at Ban-Me-Thuot is representative of the "red soils" of SVN. The Committee would have liked to conduct similar work for alluvial soils, since they represent the soils of the main agricultural region of the country, the Mekong Delta. However, with the time and mampower available this proved beyond our capacities. It would also have been desirable to repeat all experiments for a second year, in order to gain some insight about annual variations, but this was not possible either, because of the time limitation under which we were working. It should be realized, however, that little critical research involving quantitative studies of the persistence of herbicides in the tropics has been done. Thus, the information pertinent to the situation in SVN collected by the Committee represents, despite its limitations, a significant contribution of new knowledge to this general problem.

The results of the Philippines experiment are illustrated in Figure 2, those of the Ban-Me-Thuot experiment in Figure 3. For the Philippines experiment, only the data for the third series (herbicide application and first planting at the start of the rainy season) are shown. In the first series (herbicide application and first plantings in the dry season, with artificial irrigation) the time course of herbicide disappearance was quite similar to the pattern of the third,

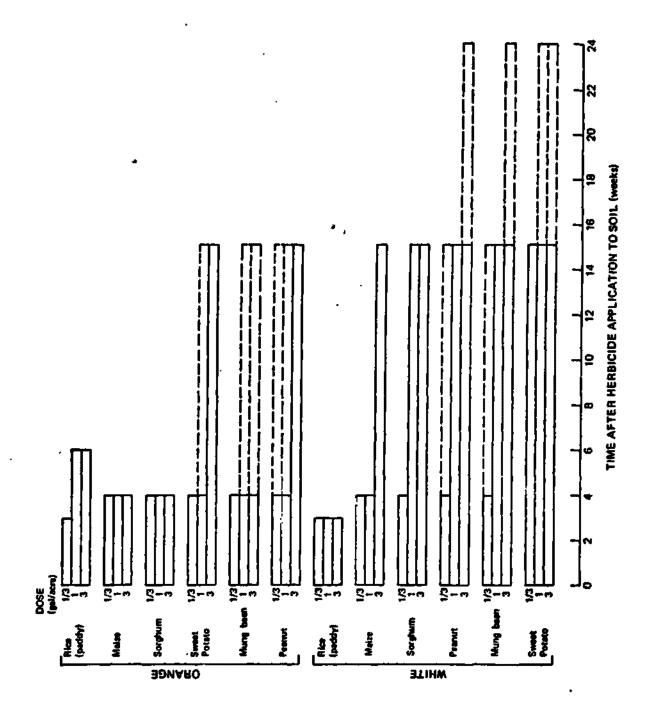


FIG. 2. The course of disappearance of the effects of herbicides on selected crops grown on soil treated with 750. 2. The course of disappearance of the effects of herbicides on science crops grown on soil treated with 3, 1, and 1/3 gal/acre of Agents Orange or White. Experiment at Alabang, Philippines.

Bars = time in weeks from herbicide application to the soil to that sequential sowing or planting where effects of herbicides on murvival and growth or yield (solid bars) and herbicide symptoms (broken bars) were no longer observable. (Lack of a broken bar = herbicide symptoms either not evident, or disappearing at same time as herbicide effects on survival, etc.) For further explanation, see text, Table V, and Figure 1.

Paddy rice (variety IR-20, one of the "miracle varieties" produced by the International Rice Research Institute) was planted as 3-week old murgery seedlings; sweet potato (local variety) as cuttings; maize (sweet corn, varieties PH 801 and UPCA Synthetic #1 and #2), morghum (variety Cosor #2), mang bean (variety CES #14) and peanut (unknown varieties) as seeds. Where varieties are known, the material was supplied by IRRI.

seeds. Where varieties are known, the material was supplied by IRRI.

Criteria for yield, survival and growth: rice - grain yield; sweet potato - survival and length of longest shoot; other grops -ssurvival and plant weight (fresh) about 4 weeks after planting.

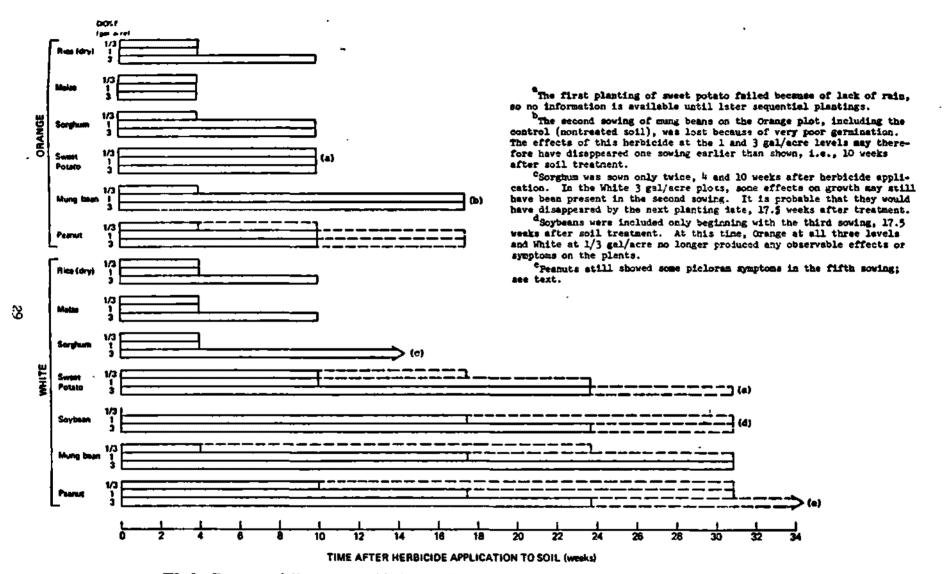


FIG. 3. The course of disappearance of herbicide effects on selected crops grown on soil treated with 3, 1, and 1/3 gal/acre of Agents Orange or White. Experiment at Ban-Me-Thuot, SVH. Bars = time in weeks from herbicids application to the soil to that sequential sowing or planting where effects of herbicides on survival and growth or yield (solid bars) and herbicide symptoms (broken bars) were no longer observable. (Lack of a broken bar - herbicide symptoms either not evident, or disappearing at same time as herbicide effects on survival, etc.) For further explanation, see text, Table V, and Figure 1. Sweet potato was planted as cuttings, the other crops as seeds. All crops were local varieties of unknown origin.

Main criteria used to assess herbicide effects: sweet potato - number of surviving plants and length of longest shoot; other crops - number of survivors and weight of plants (fresh), in all cases 4-5 weeks after planting.

which means, of course, that the herbicide effects disappeared at correspondingly earlier calendar dates. In the second series (herbicide application in the dry season, but planting delayed for four months until the start of the wet season) the effects of the herbicides disappeared in general at the same time as in the third plantings. However, as long as symptoms were discernible they were somewhat more pronounced in the second than in the third series, indicating a somewhat greater herbicide persistence. The reason for this is not clear; one possibility is that because of lack of competition by water the herbicide molecules were more effectively adsorbed to the soil particles and therefore somewhat less accessible to later loss and degradation.

From Figures 2 and 3, the following conclusions can be drawn:

- 1. The herbicidal effects persisted in different crops for different lengths of time; i.e., the crops differed in their herbicide sensitivity. The three cereals (rice, maize, sorghum) were less sensitive than the broadleaf crops (mung bean, soybean, peanut, sweet potato) because the recorded deleterious effects stopped sooner.
- 2. The effects of Agent White lasted longer than those of Agent Orange. The main difference between the two agents is that White contains picloram while Orange contains 2,4,5-T; the observed effects can be attributed to the greater persistence of picloram.
- 3. In the Ban-Me-Thuot experiment, the persistence of the two agents, and particularly of Agent White, was greater than in the Philippines experiment. Symptoms of picloram injury were still evident in peamuts in our last planting at Ban-Me-Thuot, made about 31 weeks after herbicide application to the soil. As this planting was completed at

the onset of the dry season, and as the Philippines experiment, second series (herbicide application to soil during the dry season, plantings lelayed until the wet season) showed that the herbicides persist throughout a dry season, it is possible that some picloram symptoms might have been found if peamuts had been planted again after the end of the dry ceason. The reasons for the difference in herbicide persistence between the two experiments may be due to any one or more of the following factors: (a) use of different varieties; (b) different soils; (c) lower temperature and less precipitation at Ban-Me-Thuot as compared to Alabang: rainfall during the period of the experiments at Ban-Me-Thuot was about 64 in., at Alabang about 90 in. including one typhoon with 7.25 in. in one day, and another with 23.5 in. in two days.

The results of our experiments, in their entirety, are in full agreement with past experience on the characteristics of 2,4-D, 2,4,5-T, and picloram. Specific and varietal differences in herbicide sensitivity are very well known. Indeed, the difference in the response of grasses and of many broadleaf plants to these compounds are the basis of most of their agricultural uses. Greater persistence of picloram, as compared to 2,4-D and 2,4,5-T, is also well established, and so is the influence of soil and climatic conditions on the disappearance of herbicides.

More important than these variations is the fact, clearly brought out in both experiments, that even though the soil received the massive dose of 3 gal/acre, the herbicides did not affect growth, even of highly sensitive crops like the legumes, for more than about 30 weeks. Even if peanut plantings at Ban-Me-Thuot should show some picloram symptoms one year after soil treatment, it should not be overlooked that effects on

growth and survival had disappeared after 17.5 weeks. It should also be appreciated that our results are overestimates in two respects. First, although the highest dose of herbicides used in our experiments, 3 gal/acre, was that used on the military herbicide missions, it is considerably in excess of what would in most cases reach the soil at least on a first mission over a particular region, when a major part of the herbicide would be intercepted by the vegetation and never reach the soil in an active form. Second, if herbicide effects were present in a planting that was made four weeks after the soil treatment and observed for another four weeks, but were absent in the next planting, made 15 weeks after the soil treatment (e.g., the effects of Agent White on survival and growth of peanuts in the Philippines experiment), this result is shown as "no effects after 15 weeks." However, the herbicide may in fact have dropped below the effective level for this crop any time from 8 to 15 weeks after application to the soil.

Forest Sites

Experiments with forest soils were conducted on a cleared forest site on Mount Makiling near Los Baños, the Philippines, kindly provided by the Philippine Department of Forestry, and on a site presently used as a plantation, about 27 years old, of <u>Hopea odorata</u>, a dipterocarp, at the Ea-Kmat Station at Ban-Me-Thuot. The former site consisted of two plots, 100 by 50 ft (30 by 15 m) in size, the latter of two narrower strips about 90 and 96 ft (27 and 29 m) long and 6 ft (1.8 m) wide. The plots were separated by buffer zones to exclude cross contamination of the two agents. One plot was sprayed with Agent Orange and the other wit

Agent White; the dose was 3 gal/acre, i.e., the rate used by military spray missions; and the ground was cleared of vegetation as in the experiments with agricultural soils. At Los Baños, both 10-in. (25 cm) murface samples and 30-in. (75 cm) cores were taken. At Ban-Me-Thuot, because of the dry conditions, the soil was very hard and only surface samples could be taken except on the last sampling occasion. Residues were determined by chemical methods alone; the results were, however, in agreement with observations on natural revegetation of the sprayed plots.

The results of the Los Baños experiment are shown in Figure 4. those of the Ban-Me-Thuot experiments in Figure 5. It can be seen that both 2,4,5-T and picloram disappeared from the soil quite rapidly, but picloram faded more slowly (it must be remembered that the initial dose of picloram was only 25 percent that of 2,4,5-T). The disappearance was greatest in the period immediately after herbicide application and then became relatively slower. It should be noted that the ordinate axes in Figure 4 and 5 (and likewise in Figures 6 and 7) are on a logarithmic scale; the absolute drop in the early period is thus much larger than may be apparent. For example, the picloram content in the top 10 in. of the Los Banos soil dropped from the theoretically-applied iose of 1.6 lb/acre to 0.49 lb/acre, in 13 days to 0.29 lb/acre, and in 31 more days to less than 0.02 lb/acre. By the end of the experiment, 18) days after application, it had dropped relatively much more slowly, to 0.008 lb/acre. The disappearance of 2,4,5-7 was more rapid than that of picloram, considering the almost 10 times higher initial dose, but the difference was not striking, and by the end of the observations (189 days

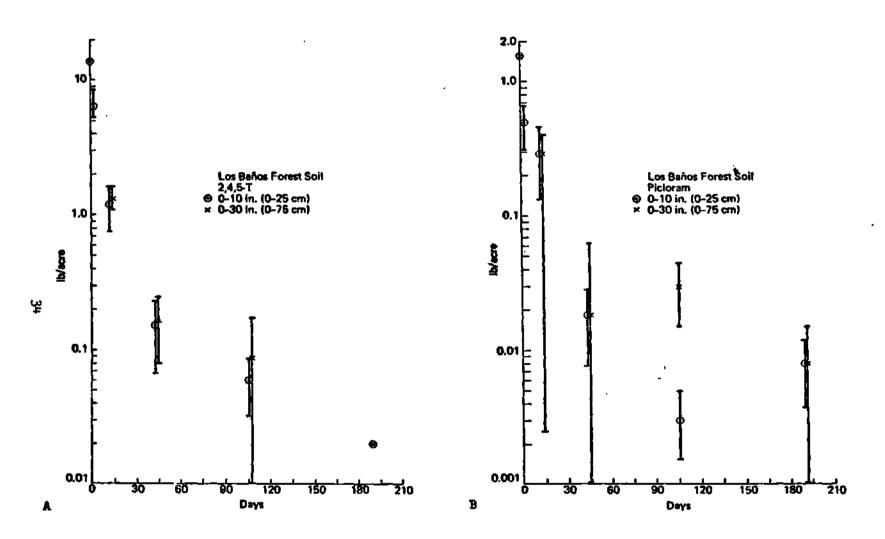


FIG. 4. Disappearance of herbicides (A, 2,4,5-T; B, picloram) from a forest soil on Mount Makiling near Los Banos, the Philippines. The applied quantities were 13 lb/acre 2,4,5-T and 1.6 lb/acre picloram. Samples were 10 and 30 in. (25 and 75 cm, respectively) deep. Abscissa - days after herbicide application, ordinate - herbicide level in soil, as lb/acre, on logarithmic scale. Vertical bars represent the 5 percent confidence limits.

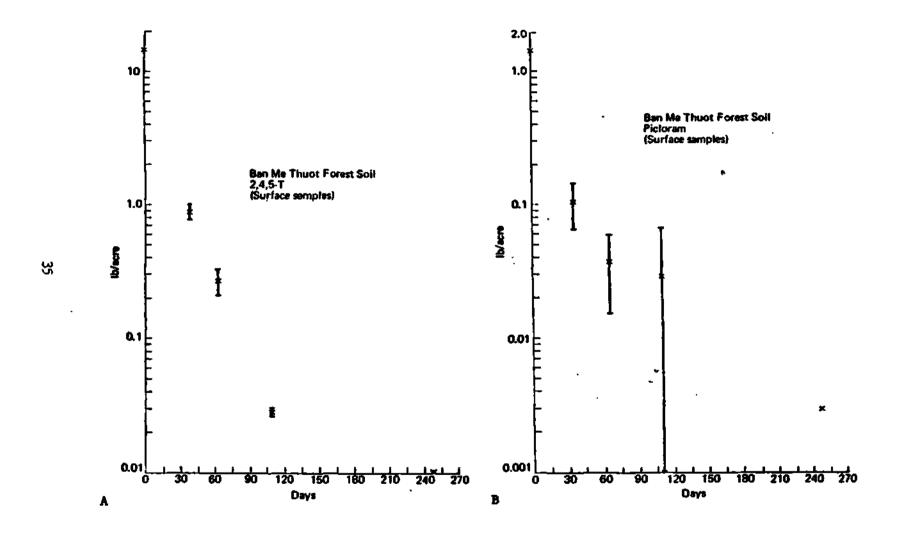


FIG. 5. Disappearance of herbicides (A, 2,4,5-T; B, picloram) from a forest soil near Ban-Me-Thmot, SVN. The applied quantities were 13 lb/acre,2,4,5-T and 1.6 lb/acre picloram. Surface samples (5 in. = 12.5 cm) only. Abscissa - days after herbicide application, ordinate - herbicide level in soil, as lb/acre, on logarithmic scale. Vertical bars represent the 5 percent confidence limits.

at Los Baños, 249 days at Ban-Me-Thuot) the levels had dropped either to slightly above or to below the detection limit. Disappearance of both herbicides in the surface and deep samples of the Los Baños experiment (0-10 in. and 0-30 in., respectively) proceeded in a similar manner (the discrepancy on the 105th day is most probably due to variations in the samples).

As already mentioned, results of observations on revegetation of the treated plots agree with the chemical data, indicating rapid disappearance of both 2,4,5-T and picloram (and of 2,4-D). At Mount Makiling, 3.5 months after the herbicide applications, both the Orangeand the White-treated plots had been fully revegetated, with a major component of broadleaf herbaceous plants including wild tomatoes. The latter -- a species highly sensitive to all three herbicides used -- had produced ripe fruits and must have started growth two months if not earlier after herbicide application. Two months later, i.e., 5.5 months after herbicide application, the plots were covered mainly with grasses that had largely replaced the broadleaf species, and numerous (unidentified) tree seedlings were present in the grass. The only possible herbicide effect still noted was an off-color individual of Philodendron sp. in the White plot. Otherwise, the treated plots were indistinguishable from the surrounding vegetation on nontreated soil. At Ban-Me-Thuot, the Orange-treated plot was at the last observation (249 days after treatment) fully revegetated with the same species that occurred in the untreated surrounding areas; the White-treated plot was still sparsely vegetated, but was being actively recolonized from the untreated areas.

Was, rove

The experiments with mangrove soils were performed in a mangrove area at Chi-Linh near the city of Vung-Tau. This area was within the perimeter of the National Popular Forces Training Center; permission for the experiments was granted by the Commander of the Center and the City Council of Vung-Tau. The exact elevation of the experimental plots is not known, but they appear to be quite frequently flooded at high tide. On all days we visited the area we observed either flooding or evidence of recent flooding.

For the initial experiment, an area 174 by 96 ft (about 50 by 30 m) was cleared of all vegetation and divided into three parts, each by 48 ft (about 30 by 15 m), separated by 15 ft (4.5 m) buffer strips. one of the outer parts was sprayed with 3 gal/acre of Agent Orange, the other with the same amount of Agent White; the center part remained untreated as a control. Spraying was carried out at low tide, when the soil was dry. Soil surface samples were taken for the first time one Lay (two tides) after the spraying and sampling of both surface samples and cores was repeated five times: 20, 40, 72, 119, and 201 days after spraying. Seedlings of two major mangrove species, Rhizophora apiculata and Ceriops tagal, were planted in groups of 100 at the time of the second, third, fourth, and fifth soil sampling and were observed about 29. 35, and 50 weeks after the date of spraying. The number of groups was originally six per treatment, but in the Orange plot some groups were on the margin of the sprayed area and were discounted, reducing the comber of some plantings to four. The results of this experiment, instructed as "Mangrove Cleared," are shown in Figures 6 and 7.

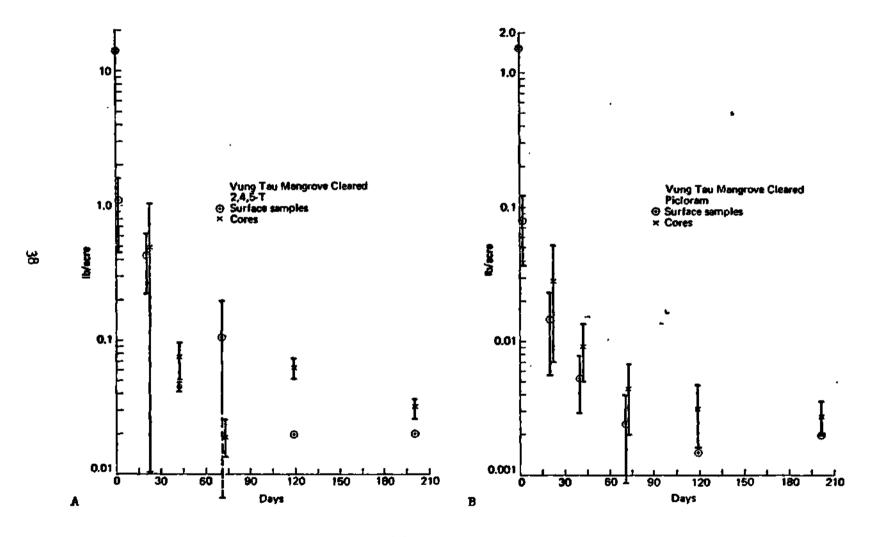
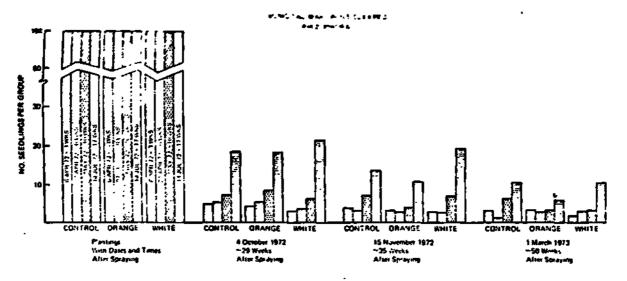


FIG. 6. Disappearance of 2,4,5-T (A) and picloram (B) from cleared mangrove soil. 2,4,5-T was applied at 13 lb/acre, picloram at 1.6 lb/acre. Surface samples were taken with 5-in. high metal cans, cores with a soil sampler 30 in. long, but the cores were usually shorter because of compacting and because of occasional loss of part of the core. Abscissa - days after herbicide application, ordinate - herbicide level in soil, as lb/acre, on logarithmic scale. Vertical bars represent the 5 percent confidence limits.



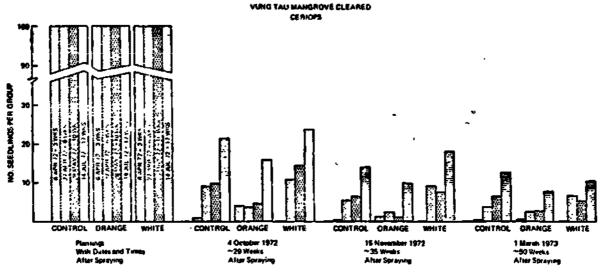


FIG. 7. Survival of <u>Khizophora</u> and <u>Ceriops</u> seedlings on cleared mangrove soil treated with Agent Orange (3 gal/acre) or Agent <u>Khite</u> (3 gal/acre), or untreated (control). On the left, the situation at the start of the consecutive plantings (100 seedlings per group) is shown; going to the right, the survival at different observation dates. At any one observation date, compare plantings of the same date, e.g., the April 6 control plantings with the plantings on Orange- and on White-treated soil of the same date, and similarly with the April 27, the May 28, and the July 14 plantings.

Figure 6 illustrates the disappearance of 2,4,5-T and picloram from the soil. The trend is quite similar to that found in the forest soils (see Figures 4 and 5): an initial rapid rate of disappearance that falls off with time. The very marked drop one day after spraying, apparent especially in the case of picloram, may be in some part due to washing out by the tide. Also, particularly in the case of picloram, the cores contain consistently higher levels of herbicide than the surface samples, suggesting that the latter had penetrated into subsurface layers and possibly further. The levels of both herbicides 201 days after spraying were either near the lowest limit of detection, or below.

Figure 7 summarizes the results of the planting experiments. Two features stand out.

First, survival was low. Twenty-nine weeks after spraying, only between about 3 and 20 percent of the <u>Rhizophora</u> seedlings were still alive, the later plantings doing relatively better than the earlier ones. Most of the seedlings of the earliest <u>Ceriops</u> planting were dead, but this was mainly because they were transplants from a prepared bed; they had already formed roots and did not survive the shock of transplanting. In the later plantings, seedlings were collected from neighboring trees and survival was better. The decline in survivor numbers continued, although at a slower pace, to the last observation. One reason for seedling death is most probably injury by crabs; seedlings with bitten roots were found partially pulled into the soil. However, we are in no position to say whether crab damage is a major or minor cause of the seedling loss observed.

Second, even in the earliest planting (made three weeks after

gra/ing and when the herbicide content of the soil was still 0.42 to 0.4. It/acre of 2,4,5-T and 0.014 to 0.029 lb/acre picloram) there was ifference in survival between the seedlings on the Orange, the White, and the control plots. For example, on the October 4 observation date, the survival in the April 6 planting of Rhizophora on the control plot was 4.7 percent, on the Orange plot 4.2 percent, and on the White plot 2.7 percent; for the July 14 planting the values were 18.7, 18.5, and 21.7 percent, respectively. By the last observation date, the values in the April 6 planting had dropped to 3.0, 3.0, and 1.6 percent, respectively, and in the July 14 planting to 10.4, 6.0, and 10.7 percent, respectively. But in no case were there large differences between the control, Orange, and White plots within plantings of one and the same date; that is, there was no effect of herbicide residues on establishment of Rhizophora and Ceriops seedlings.

Because of this result, which was somewhat surprising in view of the sensitivity of mangrove communities to aerial application of herbicite, and because of the poor seedling survival, the experiment was rejeated; however, it was modified to simulate conditions in an intact mangrove that had not been cut or sprayed with herbicides. For this jurpose, 27 microplots of one square m (1.2 yd²) were cleared of vegetation. Eighteen were hand-sprayed, nine with Agent Orange and nine with Agent White at the same rates as in the "Mangrove Cleared" experiment; the last nine remained as untreated controls. Soil surface samples and cores were taken 26 or 28, 45, 82, and 138 days after spraying; Rhizophora and Ceriops seedlings were planted 4, 6.5, and about 12 weeks after spraying, on each occasion 40 seedlings per plot, three plots each for

Orange, White, and control.

Figure 8 shows that disappearance of the herbicides (2,4,5-T and picloram) proceeded much as in the "Mangrove Cleared" experiment. Perhaps it occurred a little more rapidly, since 2,4,5-T had dropped below the detection limit by 138 days in both surface samples and cores (in the former, it was undetectable even at 82 days) while in the "Mangrove Cleared" experiment traces were still detectable in core samples after 201 days. It should be noted that the soil of the microplots site contained more sand than that of the "Mangrove Cleared" experiment; tidal flooding may also have been somewhat less frequent.

Figure 9 illustrates the behavior of seedlings. Survival was much better than in the "Mangrove Cleared" experiment -- and in Rhizophora better than in Ceriops. Compare particularly the November 15, 1972 observation date in Figure 7 and the March 1, 1973 date in Figure 9; both represent a similar period after spraying (about 34 and 35 weeks. respectively). It appears that the situation in a largely undisturbed mangrove can be a good deal more favorable for the establishment of mangrove seedlings than in a relatively large, cleared area in the mangrove. With respect to the herbicide effects, however, the microplot experiment gave results quite similar to those of the "Mangrove Cleared" experiment. Although at the time of the first planting the soil still contained substantial amounts of the herbicides, and although some seedlings of this planting on the Agent White-treated plots exhibited characteristic picloram symptoms (pale leaf color, rolled-up leaf margins), the numbers of survivors in this as well as in subsequent plantings were comparable on control, Orange-treated, and White-treated plots. In other words, both

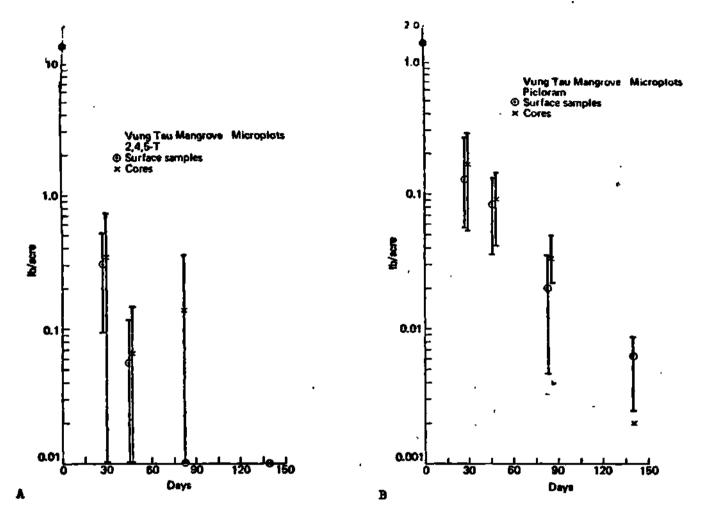
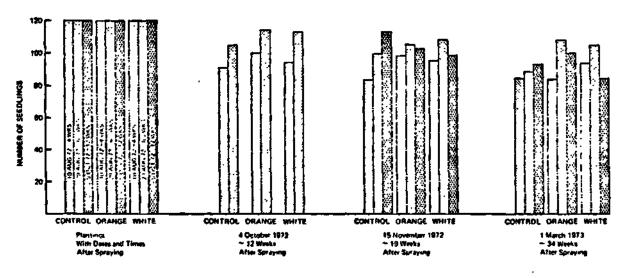


FIG. 8. Disappearance of 2,4,5-T (A) and picloram (B) from mangrove soil in small cleared plots within undisturbed mangrove. 2,4,5-T was applied at 13 lb/acre, picloram at 1.6 lb/acre. Surface samples were taken with 5-in. high metal cans, cores with a soil sampler 30 in. long, but the cores were usually shorter because of compacting and because of occasional loss of part of the core. Abscissa - days after herbicide application, ordinate - herbicide level in soil, as lb/acre, on logarithmic scale. Vertical bars represent the 5 percent confidence limits.

YUNG TAU MANGROVE MICROPLOTS RHIZOPHONA



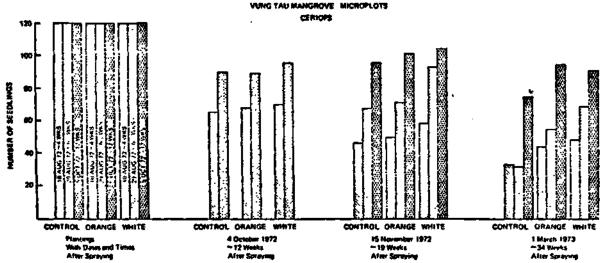


FIG. 9. Survival of <u>Rhizophora</u> and <u>Ceriops</u> seedlings in small cleared plots within undisturbed mangrove treated with Agent Orange (3 gal/acre), Agent White (3 gal/acre), or untreated (control). See legend, Pigure 7.

experiments show that three to four weeks after application to soil at the rates of 13 lb/acre 2,4,5-T and 12 lb/acre 2,4-D, or 1.6 lb/acre picloram plus 9.3 lb/acre 2,4-D, none of these herbicides impaired the establishment of mangrove (Rhizophora apiculata and Ceriops tagal) seedlings. Nor was the seedling growth, as expressed by height, different in both experiments on herbicide-treated and control plots (Table VI).

GENERAL CONSIDERATIONS OF THE DISAPPEARANCE OF HERBICIDES APPLIED TO THE SOIL IN VIETNAM AND SIMILAR ENVIRONMENTS

Comparative Patterns of Persistence in Different Soils

The disappearance pattern of phytotoxic residues from all the soils examined in the present study is similar to that found in the more extensive investigations undertaken in temperate regions. In whole core samples (Figures 4, 6, and 8), the percentage of the theoretical amount initially applied that was left in the soil by the final sampling occasion (up to 240 days after application) ranged from 0.15 to 0.23 for 2,4,5-T and from 0.12 to 0.5 for picloram. Examination of the residual phytotoxicity to selected crops (Figures 2 and 3) indicates that, for the highest rate of application, the interval required before symptoms of injury were no longer observed varied. For Agent Orange the time ranged from 4 weeks for a resistant crop such as maize to 18 weeks for a susceptible species such as peanuts. The data for Agent White were 4 weeks for maize and 31 weeks for mung bean. For peanut, at the highest doses slight symptoms of phytotoxicity were still observable at the final assessment. Comparable data from other parts of the tropics are meager

Table VI.

Average height (in.) of shoot above ground level of mangrove seedlings planted on herbicide treated and on untreated (control) plots. (Date of observation March 1, 1973)

•	Rhizophora			<u>Ceriops</u>			
Planting Date	Control	Orange	White	Control	Orange	White	
		16	_	leared" Expe	riment ^a		
May 28, 1972	16.2	15.5	16.4	11.3	10.2	10.5	
July 14, 1972	14.8	14.8	16.6	10.9	11.0	11.5	
	Microplot Experiment						
August 5, 1972	14.4	13.4	14.1	9.4	10.1	9.1	
October 10, 1972	16.5	15.8	15. 9	9.8	9.2	9.1	

a Mangrove Cleared Experiment: Herbicide application March 17, 1972. Number of plants per treatment measured between 7 and 58. Number of plants in two earlier plantings (April 6 and 27) too small for valid observations.

bMicroplot Experiment: Herbicide application July 15, 1972. Number of plants per treatment measured 32 to 45. Only first and last plantings shown.

and none exist for mangrove soils. The results of some relevant experiments have been collated in Table VII. In the Puerto Rico field study on two susceptible species the time for disappearance of phytotoxic effects was 8 weeks for a mixture of 2,4-D and 2,4,5-T and 12 to 53 weeks for a mixture of 2,4-D, 2,4,5-T, and picloram. These intervals are in the same range as those found in the present investigation. In the Puerto Rican forest soil experiment, the 0.7 percent picloram residue at the end of one year is not out of line with the range of 0.3 to 0.5 percent in Figures 4B and 5B, considering both the much higher dose (9 compared to 1.6 lb/acre) and the much longer interval before the terminal sampling occasion. For the other three sources quoted, comparisons with the data from Southeast Asia can only be tentative. If it is postulated that the shapes of the degradation curves against time are relatively independent of the initial doses, then on the basis of the data for the two forest soils (Figures 4 and 5) interpolation would predict a 90 percent loss of both 2,4,5-T and picloram within 15 days, whereas the observed intervals in Texas were 1.5 months for 2,4,5-T and 2.3 months for picloram. Similarly, the intervals recorded for a 90 percent loss under temperate conditions in Table VII again exceed those predicted for forest soils in SVN and the Philippines.

The processes by which a herbicide is lost from the soil and that hence determine its persistence can be divided into those that remove the chemical unchanged from the system, and those responsible for its decomposition within the system. The first group consists of volatilization, leaching, runoff, and uptake by plants. The second involves chemical breakdown by biological and nonbiological processes. The data

Table VII.

Disappearance of 2,4-D, 2,4,5-T and picloram from soil in warmer climates.

Herbicide and dosage

		ODSET VA CLOII		
Field Study in Puerto Rico				
(Bovey et al. 1968)	Time (in months)	for no symptoms on:		
	Soybean	Cotton		
Picloram, 6 lb/acre 2,4-D + 2,4,5-T, 12 + 12 lb/acre 2,4-D + 2,4,5-T + picloram, 6 + 6 + 3 lb/acre	6.5 2 6.5	3 2 3		
Forest in Puerto Rico (Dowler et al. 1969)	Amount left in to year (in p	op 48 in. after one percent)		
Picloram, 9 lb/acre Picloram, 27 lb/acre	o. 5.	•		
Field Studies in Texas				
(Bovey et al.1969, Bovey and Baur 1972)	Time for 90 percent or more degradation (months)			
2,4,5-T, 0.5 and 1 lb/acre Picloram, 1 oz/acre Picloram, 1 lb/acre	Less than 1.5 0.7 2.3			
For comparison, Temperate Climate Conditions (av	erage figures)			
	Time for about 90 (75-100) percent degradation (months)			
2,4,5-T ("Report on 2,4,5-T," 1971, Kearney 1970)	3.	3- 6		
Picloram, 1 oz to 1 lb/acre (Hamaker et al. 1962, Herr et al. 1966, Scifres et al. 1971, Bovey et al. 1969)		-1 6		

Observation

reported in this chapter must be interpreted in the light of (1) what is known from previous investigations of the importance of these factors on the behavior of 2,4-D, 2,4,5-T, and picloram in soil, and (2) the characteristics of soil and climate in SVN that may affect herbicide persistence.

Volatilization and Photodecomposition

The n-butyl esters of 2,4-D and 2,4,5-T, the constituents of Agent Orange, are moderately volatile (see Section II C, Part A of the Report on the Effects of Herbicides in South Vietnam) and might be expected to vaporize quickly on contact with soil or plant surfaces under tropical conditions. The ability of plants to hydrolyze esters of 2,4-D to the nonvolatile acid is well known, but some loss as a vapor from leaf surfaces before entry is a possibility. In soil, rapid hydrolysis occurs even at low moisture levels (Smith 1972); this could reduce or eliminate losses in a vapor form. Moreover, under very dry conditions adsorption of volatile herbicides by the soil surfaces is well known to reduce such losses. The salt forms of 2,4-D and picloram used in Agent White are not appreciably volatile, and significant losses by this route can be discounted. It is probable, therefore, that volatilization from soil was not of major importance.

In laboratory experiments the acids can be decomposed by the action of light, but under field conditions it is generally unlikely that such losses would be appreciable; this expectation agrees with the observations already recorded at Alabang. Here the residual toxicity of Agent Orange applied in the dry season (February 2), with the soil surface left undisturbed until crop planting on May 30 was similar to the residual

toxicity in plots sprayed on May 3 and also planted on May 30. Thus losses from soil due either to photodecomposition or volatilization are likely on theoretical grounds to have been small. Moreover, the lack of phytotoxic symptoms in susceptible crops planted in our control plots immediately adjacent to plots sprayed with Agents Orange and White suggested that volatilization was of little consequence.

Runoff

Any material applied to the soil is liable to be carried from the site of action when rain causes surface runoff and water erosion; the degree depends on the intensity of the precipitation, the soil characteristics, the nature of the surface, and topographical features. The amount of herbicide removed in the surface wash will also be dependent on the interval since application. In the present experiments the only evidence for runoff after heavy rain came from (1) the phytotoxic symptoms observed below the treated plots (which were situated on a slope in the forest soil experiment in the Philippines) and (2) from picloram symptoms on untreated plots of very susceptible crops observed after the heavy typhoon at Alabang (noted above). It has also been mentioned that in the mangrove experiment on the cleared site the herbicidal contents of the surface samples taken two tides after application may in part have been affected by tidal waters carrying away some of the surface particles.

Leaching

The proportion of a herbicide that is physically bound within the soil matrix is dependent on its physicochemical characteristics and

the nature of the soil. A combination of these properties determines the amount that is transported downwards through the soil by water percolating from the surface. This leaching action is dependent on two interacting sets of conditions. The downward movement of the soil solution will occur only when on average the amount of incoming rain exceeds the amount of water lost by evaporation from the soil and transpiration from the vegetation. The amount of herbicide that moves downward is dependent on both the freedom with which the soil solution can pass through the soil pores, and the concentration of herbicide in solution (which will be in equilibrium with the amount retained on the surfaces of the soil particles). Thus losses of herbicides will be greatest when rainfall markedly exceeds evapotranspiration, the soil is free draining, and the retentive power of the surfaces is low. Losses will be minimal (1) in the dry season, (2) when the soil is relatively impermeable, and (3) if the capacity for adsorption is high. For individual herbicides there is the further consideration that the greater the degree of binding on any one soil type the less the liability of leaching.

Against this background it would be expected that the capacity for retention would be less for the forest soils at Los Baños and Ban-Me-Thuot than for the heavy clay soil at Alabang and the estuarine muds of the mangrove experiments. It would also be expected that leaching would be least at Ban-Me-Thuot, which had the lowest rainfall over the experimental period. Since no basic data are available for the conditions of mangrove soils, the effects of the fluctuations in the water table and intermittent flooding of the surface are not predictable, but it is likely--at least during the initial phase--that each time the water table recedes from the

surface layer there will be some transfer of the herbicide to a lower depth. There is some suggestion of this in Figure 6A and B, since the cores tend to have a higher content than the surface samples.

It is very difficult to disentangle the losses caused by leaching from the losses related to the activities of microorganisms. But at least in some experiments it would seem that the component of leaching was small. For example, it is apparent that on the forest soil experiment at Ban-Me-Thuot (Figure 5A and B) the progressive disappearance of both compounds took place under conditions where, subsequent to the initial spraying, lack of rain led to steadily drier soil over the first three months; hence, there cannot have been appreciable leaching from the surface layers. Moreover, if leaching is a major component it would not be expected that in the Pran Buri Calibration Grid picloram would be still present after eight years, with the residues largely present in the top layers of the soil.

These findings are in general agreement with the literature and the expected behavior of 2,4-D and 2,4,5-T where they appear as the parent acids, which have a low solubility in water.

The extent of the leaching of highly soluble picloram is dependent on the soil type; it is seemingly most marked in sandy soils (Bovey et al. 1969). Leaching is known to occur to considerable depths, and those who have looked at depths greater than 3-4 ft have generally found traces, although higher concentrations occur near the surface. On the basis of picloram's greater mobility compared with 2,4,5-T (Helling 1971), it is puzzling to note from Table VIII that in the first 44 days the proportion of the remaining residue of picloram found in the top layer is much larger than that of 2,4,5-T.

Table VIII.

Changes in the distribution of herbicides in forest soil,
Los Baños, the Philippines.

(Figures are percent of total found at each depth)

Depth (in./cm)	13	44	105	189
	2	,4,5-T		
			* ,	
Top (0-10/0-25)	68.7	44.9	59.8	
Middle (10-20/25-50)	17.9	31.1	35.7	-
Bottom (20-30/50-75)	13.4	24.0	4.5	-
lb/acre (average)	1.37	0.16	0.09	
	Pi	cloram		
Top (0-10/0-25)	98.3	90.9	22.6	63.1
Middle (10-20/25-50)	1.1	5.5	43.8	23.4
Bottom (20-20/50-75)	0.6	3.6	33.5	13.5
lb/acre (average)	0.27	0.03	0.03	0.01

Degradation

It is well established that 2,4-D and 2,4,5-T are degraded by soil microorganisms--2,4-D very rapidly, 2,4,5-T more slowly. There is also firm evidence that repeated treatment with these herbicides accelerates the rate of breakdown. Factors that favor the growth of microorganisms, such as high temperatures, moist conditions, and a ready availability of substrates, also enhance the level of decomposition. Such studies, including the chemical pathways of degradation, have been extensively reviewed by Loos in Kearney and Kaufman (1969).

The course of degradation of 2,4-D and 2,4,5-T by soil microorganisms is well documented. At first little breakdown takes place (lag phase), then the rate builds up rapidly to a high level, which is followed by a third phase when the rate declines. The data of Figures 4A, 5A, and 6A share these common characteristics: the amount of herbicide present in the soil at first falls rapidly, but later the rate of disappearance slows down. Thus, on the basis of the similarities between these field studies and the laboratory studies of metabolic degradation, it can be postulated that both in the mangrove and forest soils microorganisms played a major role. Since, however, there was no prior information on the capacity of the microorganisms present in these types of tropical soils to decompose the more resistant 2,4,5-T, an experiment was carried out at the Weed Research Organization (Hance, personal communication) in which radioactive 2,4,5-T n-butyl ester (14C-labeled carboxyl group) was applied to both mangrove and upland soils from SVN. The results confirmed that these soils were capable of degrading 2,4,5-T to carbon dioxide in the laboratory. When the output of radioactive CC2 was plotted against

time, the curves showed the typical lag phase associated with microbial degradation (Audus 1964). The soil samples used for this experiment were taken from the area of the dump site in the Di-An District, the Kinh-Ngang Canal in the Ca-Mau Peninsula, and from Site #1 in the Rung-Sat Special Zone. The last two were mangrove soils.

Reference has already been made to the possibility that 2,4-D and 2,4,5-T may be decomposed by the action of light, but there are other nonbiological processes that participate such as hydrolysis, oxidation, and reduction. The surfaces of soil components may or may not catalyze these reactions; this matter requires further study.

The pathways of disappearance of picloram are not adequately understood. The available evidence suggests that photodecomposition, leaching, and microorganisms are all involved, with the latter probably playing a major role (Upchurch 1973). Thus there is supporting evidence that the losses of picloram with time shown in Figures 4B, 5B, and 6B are associated with the activities of microorganisms.

To conclude, the data collected by the Committee from experiments and soil samples in SVN, the Philippines, and Thailand all indicate that the general disappearance pattern of the three herbicides is in line with that well known for temperate regions. Moreover, all information the Committee was able to gather locally from farmers, village and district officials, and agricultural advisers indicated that crops could be grown again with no reductions in yield or other ill effects the year following one or more herbicide missions. If crops were not grown it was either because of lack of security, or apprehension that the herbicide treatment might make the produce unfit for consumption.

GENERAL CONCLUSIONS

Several deficiencies in our studies have been mentioned before. We were able to collect soil samples in only one forest area in SVN that had been sprayed during the war; we were unable to make collections in forest areas that had received the relatively heaviest sprayings. We were also unable to repeat our own experiments for a second year, and to conduct them on the other major soil type of SVN, the alluvial soils.

However, these deficiencies are counterbalanced by two important considerations. First, our evaluation of persistence included different agricultural and forest soils (in SVN and the Philippines) as well as mangrove soils. The sites were selected because local conditions happened to be favorable and, except for trying to take samples in heavily sprayed areas, and to include soils from vegetation types most extensively subjected to military herbicide sprays, no attempt was made to give preferential coverage to a particular soil type or any other factor. Second, our findings, at least those on the fate of herbicides in soils, are in excellent agreement with general experience on this problem.

Thus viewed, our data possess considerable internal consistency and, in our opinion, permit a number of general conclusions, namely:

- The behavior of herbicides in the soils of Vietnam and the Philippines is similar to that reported for soils elsewhere.
- 2. Only where herbicides (2,4-D, 2,4,5-T, picloram) were applied in very massive doses (the former two in the magnitude of 1000 lb/acre, picloram at 20 lb/acre: Pran Buri Calibration Grid; see Table II), are they still in part present in concentrations that are above the threshold

likely to induce phytotoxic symptoms in some species.

- 3. Where applied to mangroves at total doses approaching 100 lb/acre of 2,4-D and of 2,4,5-T, or 3 or more lb/acre of picloram, the herbicides may still be present at low levels. Although the amounts present varied between sampling sites, the levels were such that the likelihood of damage to crops that could be grown under these conditions can be discounted. They were far below the levels that, in our own experiments, had no effect on the establishment of seedlings of Rhizophora apiculata and Ceriops tagal. Moreover, seedlings and young plants of mangrove species that we observed in heavily sprayed areas of the Rung-Sat, where 2,4,5-T and/or picloram were still detectable by chemical methods, did not exhibit any herbicide symptoms.
- 4. In areas subject to one or two herbicide missions 1.5 years before sampling, no phytotoxic residues could in general be detected.
- 5. Our results indicate that after a single application of Agent Orange, even where conditions are such that all the spray reaches the soil, crops sensitive to 2,4-D or 2,4,5-T may be safely sown after four to six months of wet weather; after an application of Agent White under the same conditions, resistant plants like rice and maize can also be safely planted four to six months after application. In this connection, it is appropriate to point out once more that the dosage used in our experiments, i.e., about 6 or 12 lb/acre of 2,4-D and 2,4,5-T, and 1.5 lb/acre picloram, applied to the bare soil, was considerably higher than the dosage that would have reached the soil when the forest or mangrove sites were sprayed for the first time because of interception of the spray droplets by the canopy.

6. Claims that the herbicides as they were used during the war have rendered the soil "sterile," permanently or at least for prolonged periods, are without any foundation. It should be noted that these claims were contrary to all existing information for the herbicides in question.

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